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(71)Applicant : NGK INSULATORS LTD

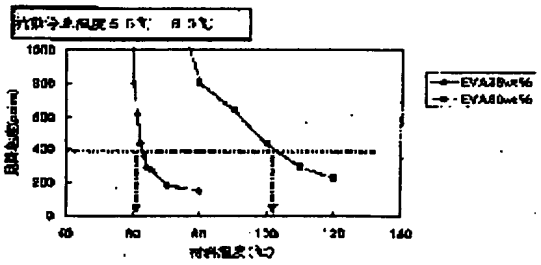
(72)Inventor : KATO SHIGEKI
HIRAI SADAAKI
KAWAE TAKAYUKI

(54) HONEYCOMB FORMED BODY AND MANUFACTURING METHOD THEREOF

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a honeycomb formed body which can be mass-produced without impairing product quality and has an improved shape retention and a partition wall of a small thickness, and a manufacturing method thereof.

SOLUTION: The honeycomb formed body is manufactured by extruding a mixture of material powder and a forming binder, and a mixture of wax and a thermoplastic resin is used as the forming binder. The mixture ratio of the thermoplastic resin in the forming binder is made 5-50 wt.%.



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CLAIMS

[Claim(s)]
[Claim 1] The honeycomb Plastic solid which carries out extrusion molding of the mixture of raw material powder and a shaping binder, changes, and is characterized by being the honeycomb Plastic solid using the mixture of a wax and thermoplastics as a shaping binder, and the mixing ratio of the thermoplastics in this shaping binder being 5 - 50wt%.
[Claim 2] The honeycomb Plastic solid according to claim 1 whose mixing ratio of the thermoplastics in this shaping binder is 20 - 40wt%.
[Claim 3] The honeycomb Plastic solid according to claim 1 or 2 this whose raw material powder is ceramic powder.
[Claim 4] The honeycomb Plastic solid according to claim 3 this whose raw material powder is cordierite presentation preparation powder.
[Claim 5] The honeycomb Plastic solid according to claim 1 or 2 this whose raw material powder is metal powder.
[Claim 6] A honeycomb Plastic solid given in any 1 term of claims 1-5 whose thickness of a septum is 25-100 micrometers.
[Claim 7] A honeycomb Plastic solid given in any 1 term of claims 1-6 used as catalyst support for automobile exhaust purification.
[Claim 8] The manufacture approach of the honeycomb Plastic solid characterized by being the manufacture approach of a honeycomb Plastic solid given in any 1 term of claims 1-7 which carry out extrusion molding of the mixture of raw material powder and a shaping binder, heating and carrying out extrusion molding of this mixture to molding temperature, and subsequently carrying out cooling solidification of the moldings.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the honeycomb extrusion-molding object used as catalyst support for automobile exhaust purification etc., and its manufacture approach.
[0002]
[Description of the Prior Art] In recent years, it is in the inclination for emission control to be tightened up every year, from consideration of an environmental problem, and the emission-gas-purification catalyst is asked for improvement in the purification engine performance that it should correspond to this. On the other hand, from the field of engine development, orientation of low fuel consumption and a high increase in power is shown notably, and the emission-gas-purification catalyst is asked also for reduction of a pressure loss that it should correspond to such a situation.
[0003] Then, raising permeability and reducing a pressure loss by making thickness of the septum of a honeycomb structure object thin, in order to solve such a problem, moreover the emission-gas-purification catalyst itself was lightweight-ized, heat capacity was reduced, and the motion which raises the purification engine performance at the time of warming up has become strong. Specifically, the 2-mil article whose thickness of a septum it is 50 micrometers that the 6-mil article whose thickness of a septum is 150 micrometers had now is becoming in use conventionally. [in use] In addition, honeycomb structure means the structure which divided many cels with the septum.
[0004] Moreover, using what mixed raw material powder, such as ceramic powder and metal powder, with the binder etc., using the mouthpiece with which the grid-like slit was formed, a honeycomb structure object is fabricated by extrusion molding, and, subsequently is usually manufactured by drying and calcinating. Conventionally, as a binder used for extrusion molding of a honeycomb structure object, the water-soluble, thermosetting methyl cellulose system binder has been used.
[0005] However, since the width of face of the slit of the shape of a grid formed in the mouthpiece also becomes small with the formation of a thin wall of a septum, it is necessary to use for shaping of a honeycomb structure object the fluid high binder which can flow into such a mouthpiece promptly. Moreover, since the reinforcement of a moldings to the extent that it came out of the mouthpiece becomes small with the formation of a thin wall of a septum and it becomes easy to deform with one's weight, it is necessary to use the high binder of firmness which comes out of a mouthpiece and is solidified soon.
[0006] Therefore, a degree of hardness is high, using the plastic matter excellent in firmness, a honeycomb structure object is fabricated, or a degree of hardness is low and fabricating a honeycomb structure object using the plastic matter which is rich in a fluidity has been performed.
[0007]
[Problem(s) to be Solved by the Invention] However, since the plastic matter with a high degree of hardness was lacking in a fluidity, while it did not flow into the mouthpiece easily, and could not aim at improvement in productive efficiency and it piled up the count of shaping since compacting pressure became high, it had the problem of a mouthpiece having deformed or wearing out.
[0008] Moreover, when a plastic matter with a low degree of hardness is used, in order to give reinforcement to the moldings which came out of the mouthpiece, it is necessary to carry out heat gel solidification of the binder by dielectric drying. However, in order to perform conveyance to a dielectric drying machine, guessing an air current from the moldings bottom so that a moldings may not deform with its weight, the problem that the crack by desiccation arose was in the part of the moldings which an air current hits.
[0009] Then, artificers are indicating previously the honeycomb Plastic solid which can control the rise of

compacting pressure in 2000 to application-for-patent 130446 specification, maintaining firmness by adopting thermoplastics as a shaping binder and specifying the mixing ratio of a wax and thermoplastics as this ingredient. although excelled in the moldability which compacting pressure was boiled markedly, and was stopped compared with old it, and the honeycomb Plastic solid also equipped with the firmness of need extent, it was what the room of amelioration is in firmness, and the mixing ratio is still examined, and is expected an improvement of gestalt stability.

[0010] The place which this invention is made in view of the trouble and the point that amelioration is desired further of the conventional technique mentioned above, and is made into the purpose is to offer the honeycomb Plastic solid with the thin thickness of a septum which can mass-produce without spoiling product quality still more certainly, and its manufacture approach.

[0011]

[Means for Solving the Problem] That is, extrusion molding of the mixture of raw material powder and a shaping binder is carried out, and it changes, and it is the honeycomb Plastic solid using the mixture of a wax and thermoplastics as a shaping binder, and the honeycomb Plastic solid characterized by the mixing ratio of the thermoplastics in this shaping binder being 5 - 50wt% is offered.

[0012] As for the mixing ratio of the thermoplastics in a shaping binder, at this time, it may be still more desirable that it is 20 - 40wt%, and the raw material powder to be used may be ceramic powder or metal powder, such as cordierite presentation preparation powder. Moreover, as for the above-mentioned honeycomb Plastic solid, it is desirable that the thickness of a septum is 25-100 micrometers.

[0013] The above-mentioned honeycomb Plastic solid may be used as catalyst support for removing harmful matter and dust from automobile exhaust.

[0014] Moreover, according to this invention, it is the manufacture approach of the above-mentioned honeycomb Plastic solid which carries out extrusion molding of the mixture of raw material powder and a shaping binder, and after heating the above-mentioned mixture to molding temperature and carrying out melting of the shaping binder, the manufacture approach of the honeycomb Plastic solid which carries out extrusion molding and subsequently carries out cooling solidification of the moldings is offered.

[0015]

[Embodiment of the Invention] In this invention, although a honeycomb Plastic solid carries out extrusion molding of the mixture of raw material powder and a shaping binder and it is manufactured, thermoplastics is used for a shaping binder. Although fused by applying heat, since it can change the viscosity of a shaping binder freely according to temperature conditions, by choosing proper temperature conditions, thermoplastics can acquire a desired fluidity, and it can mass-produce a honeycomb Plastic solid, without spoiling productive efficiency.

[0016] Moreover, since cooling solidification is carried out, before a moldings causes deformation by its weight by quenching immediately the moldings which came out of the mouthpiece with the cold blast below cold water and the congealing point etc., the fused thermoplastics can solidify a binder easily and can secure the firmness of a moldings.

[0017] In order to use the shaping binder of nonaqueous solubility in this invention, desiccation of a Plastic solid becomes unnecessary. In the case of extrusion molding using a water-soluble binder, the air bubbles in the mixture (henceforth raw material mixture) of raw material powder and a shaping binder must be removed by vacuum degassing, but since desiccation does not take place when the shaping binder of nonaqueous solubility is used to the hard soil produced by local desiccation in vacuum degassing causing blinding of a mouthpiece, the blinding of a mouthpiece cannot happen but productive efficiency can be raised also from this viewpoint. In addition, when the shaping binder of nonaqueous solubility is used, vacuum law evasion is not indispensable.

[0018] In this invention, as a shaping binder of nonaqueous solubility, although a wax and thermoplastics are used, as a wax, paraffin wax, a micro crystallin wax, etc. are used suitably, and, specifically, common thermoplastics, such as EVA, polyethylene, polystyrene, a liquid crystal polymer, and engineering plastics, is suitably used as thermoplastics. Moreover, in this invention, one sort may be used independently, and the aforementioned shaping binder may be combined two or more sorts, and may be used. Furthermore, assistants, such as a coupling agent, lubricant, and a dispersant, may be added and used for the above-mentioned shaping binder.

[0019] Moreover, when using what mixed thermoplastics with the wax as the above-mentioned shaping binder in this invention, as for the mixing ratio of the thermoplastics in a shaping binder, it is desirable 5 - 50wt% more preferably that it is 20 - 40wt%.

[0020] In the honeycomb Plastic solid using thermoplastics, the important points which see firmness are the

temperature at the time of dissolving and kneading the charge of an admixture of raw material powder and a shaping binder, and extruding it (this temperature is hereafter called "molding temperature".), and extent of the difference of the temperature which that extruded Plastic solid begins to solidify. The difference of this temperature is called "temperature sensitivity", and the firmness of an extrusion-molding object will improve, so that a temperature sensitivity is so sensitive that the difference of temperature is small.
[0021] The difference of the mass ratio of the shaping binder to raw material powder, the wax in a shaping binder and the mass ratio of thermoplastics, or the melting point of a wax and thermoplastics etc. influences this temperature sensitivity. If a temperature sensitivity is made sensitive, while the firmness of an extrusion-molding object will improve, it becomes possible to make an extrusion rate quick, and the productive efficiency of a honeycomb Plastic solid will improve remarkably.
[0022] Here, using EVA as thermoplastics, the mixing ratio of the thermoplastics in a shaping binder takes EVA35% and EVA60% of extrusion-molding object for an example, and explains the effectiveness of a temperature sensitivity concretely. Drawing 1 makes temperature a parameter using the Shimadzu descent type flow tester, and others show the apparent viscosity measured on certain conditions. If extrusion temperature is fixed and a temperature sensitivity is compared, as for the molding temperature at the time of 400poise(s), apparent viscosity will go up from drawing 1 to near 100 degree C in the EVA60% article to being near 60 degree C in an EVA35% article, for example. On the other hand, the temperature (henceforth "flow halt temperature") which discovers each firmness is near 55 degree C in 35% article, and is near 60 degree C in 60% article. Therefore, in this case, as shown in Table 1, the direction of that whose mixing ratio of the thermoplastics in a shaping binder is 35% will be excellent in a temperature sensitivity, and the firmness of an extrusion-molding object will be excellent.
[0023]
[Table 1]

熱可塑性樹脂	成形温度	流動停止温度	温度差（感温性）
35wt%	60℃	55℃	5℃
60wt%	100℃	60℃	40℃

[0024] Although explained in detail in the example mentioned later, if the mixing ratio of thermoplastics exceeds 50%, molding temperature will rise, firmness falls and the danger that an extrusion-molding object will deform comes out. If the mixing ratio of thermoplastics exceeds 40%, although firmness will become good and configuration grant will become easy, an extrusion rate will fall and productivity will fall. Moreover, although configuration grant will become easy if [if the mixing ratio of thermoplastics considers as less than 5%, the bonding strength of a shaping binder will decline and configuration grant of an extrusion-molding object will become difficult, and] less than 20%, since a temperature sensitivity becomes very sensitive, the temperature control at the time of production will become severe, consequently productivity will fall.
[0025] In this invention, although extrusion molding of the mixture of raw material powder and a shaping binder is carried out, the addition of the shaping binder in the above-mentioned mixture changes with classes of shaping binder to be used, and adds the amount which can acquire a desired fluidity.
[0026] In this invention, as raw material powder used for manufacture of a honeycomb Plastic solid, although ceramic powder or metal powder is used suitably, with ceramic powder, the powder of the ceramic which are nitrides, such as oxides, such as cordierite presentation preparation powder, an alumina, and a mullite, and silicon nitride, silicon carbide, alumimium nitride, can be used. Powder, such as Fe, Cr, nickel, and aluminum, can be used in metal powder.
[0027] In this invention, although a honeycomb Plastic solid is manufactured by extrusion molding, especially if it is the facility which can do heating and pressurization as a kneading facility, it will not be limited, but can use a common kneader, a pressurized kneader, a 2 shaft continuation kneading extruder, etc. Moreover, especially if the shaping equipment used by this invention can do heating and pressurization and has an extrusion function, it will not be limited, but a plunger type extruder, a kneading machine, an injection molding machine, a 1 shaft continuous extrusion machine, a 2 shaft continuation kneading machine, etc. can be used for it. Furthermore, in this invention, the 2 shaft continuation kneading extruder as for which kneading and shaping are made to coincidence can also perform kneading and shaping to coincidence. In continuous molding, although the atomization of a binder is needed, as the atomization approach, a spray dryer and frost shattering are applicable, for example. Moreover, there is especially no limit in the heating means of shaping equipment, for example, you may heat at a heater, and may heat by

thermal circulation using an oil etc.
[0028] In this invention, although self-weight deformation of a moldings, especially cel crushing are prevented by carrying out cooling solidification of the moldings which came out of the mouthpiece, there is especially no limit in the cooling approach, for example, approaches, such as water cooling by air cooling and the atomizer, can be used. Moreover, it may be made to fall underwater and you may quench a moldings. In addition, depending on molding temperature, an extrusion rate, and an EVA addition, especially compulsory cooling is unnecessary, and room temperature cooling is enough as it. Moreover, although a moldings is horizontally extruded from an extruding press machine, it goes caudad and you may make it usually extrude a moldings with a vertical mold making machine.
[0029] From a viewpoint which reduces the stress at the time of cooling, the small thing of the difference of molding temperature and cooling temperature is desirable, and it is [that the cooling temperature immediately after extruding from a mouthpiece should just be temperature which a shaping binder solidifies / a cooling rate] good. [of the later one] It is because a possibility of generating a crack defect is in the cel section which is an internal elevated temperature when only a front face is hardened firmly, since thermoplastics carries out cooling solidification by temperature fall.
[0030] In this invention, especially a limit may not be in the cross-section configuration of the cel of a honeycomb Plastic solid, and you may be polygons, such as a triangle, a square, and a hexagon, a round shape, etc. Moreover, the consistencies of a cel may be 300 - 2000 cel / inch 2.
[0031] In a low-temperature field, baking of a Plastic solid is performed by choosing conditions without generating of a cel piece in consideration of the scattering curve of a shaping binder, and is performed in an elevated-temperature field by choosing the conditions which can give target properties, such as porosity and coefficient of thermal expansion. Moreover, cleaning and baking of a honeycomb Plastic solid should just choose an inert atmosphere and the vacuum middle class suitably among atmospheric air according to the class of raw material powder. For example, after degreasing in atmospheric air in the case of the cordierite presentation mixing powder which is oxide, it calcinates in atmospheric air and continuous furnaces, such as a single furnace or a tunnel, usually perform cleaning and baking to coincidence.
[0032] When using for the catalyst for automobile exhaust the honeycomb structure object manufactured as mentioned above, after forming a gamma alumina layer in a cel path internal surface and making noble-metals components, such as platinum which is a catalyst component, a rhodium, and vanadium, support in the pore of the gamma alumina layer, a catalyst can be burned at the temperature around 600 degrees C.
[0033]
[Example] Hereafter, although this invention is explained in more detail using an example, this invention is not restricted to these examples.
[0034] (Examples 1-12) Cordierite presentation mixing powder is used as raw material powder, the mixture of a wax and thermoplastics is used as a shaping binder, it has a circular end-face configuration, and the honeycomb Plastic solid whose cross-section configuration of a cel is the square of 2 mils (50 micrometers) in septum thickness, and the cel consistency 600 cel / inch 2 was manufactured. The mixing ratio of a shaping binder was made into the value shown in Table 2.
[0035] First, the shaping binder of 100 micrometers of mean diameters was added to cordierite presentation preparation powder, it kneaded with the pressurized kneader to it, and the cylindrical shape-like (cup soil) molding material was produced with the kneading machine to it so that the content of the shaping binder in 100 % of the weight of raw material mixture might become 28 mass %. Preheating was carried out to the molding temperature which shows **** in Table 2 all over a water bath after that, and it fabricated with the plunger molding machine. Molding temperature is shown in Table 2. As resin, EVA420 (made in Mitsui E. I. du Pont de Nemours Chemical, Inc.) was used, using paraffin wax (NIPPON SEIRO CO., LTD. make), a micro crystallin wax (NIPPON SEIRO CO., LTD. make), and oleic acid (the Katayama chemistry incorporated company make) as a wax of a shaping binder.
[0036] Next, the honeycomb was fabricated with the extrusion rate which was extruded with the plunger molding machine and which is shown in Table 2, and the honeycomb which came out of the mouthpiece was cooled by the approach shown in Table 2. About the acquired honeycomb Plastic solid, the cel configuration was investigated visually. A result is shown in Table 2.
[0037] (Example 1 of a comparison) The same honeycomb Plastic solid as examples 1-12 was manufactured by the same approach as examples 1-12 on the conditions shown in Table 2, using only a wax as a shaping binder.
[0038] (Example 2 of a comparison) The same honeycomb Plastic solid as examples 1-12 was manufactured by the same approach as examples 1-12 on the conditions shown in Table 2, using EVA60% as a shaping

binder.
[0039]
[Table 2]

	EVA添加量（質量%）	成形温度（℃）	冷却方法	押出速度（mm/sec）	形状付与性	セル潰れ
比較例１	0（ワックス100）	５５	室温放冷	ハニカム形状が得られず計測不可	形状付与できず	評価できず
実施例１	5（ワックス95）	５６	室温放冷	１５	若干変形	良好
実施例２	１０（ワックス90）	５７	室温放冷	２０	良好	良好
実施例３	２０（ワックス80）	５８	室温放冷	２０	良好	良好
実施例４	２０（ワックス80）	５８	室温放冷	3.0	良好	良好
実施例５	２０（ワックス80）	５８	５０℃温風冷却	４０	良好	良好
実施例６	３５（ワックス65）	５９	室温放冷	20	良好	良好
実施例７	３５（ワックス65）	６０	室温放冷	２０	良好	良好
実施例８	３５（ワックス65）	６０	５０℃温風冷却	３０	良好	良好
実施例９	３５（ワックス65）	６０	４０℃温風冷却	４０	良好	微少
実施例１０	４０（ワックス60）	６２	４０℃温風冷却	２０	良好	良好
実施例１１	５０（ワックス50）	７０	４０℃温風冷却	１０	良好	良好
実施例１２	５０（ワックス50）	８０	３０℃温風冷却	１０	若干変形	潰れ中程度
比較例２	６０（ワックス40）	１２０	４０℃温風冷却	２０	変形大	潰れ大

[0040] Configuration grant nature is good and Table 2 shows not generating cel crushing mostly, if the EVA addition which is thermoplastics is the proper range of 5 - 50 mass %. Also in it, as for configuration grant nature and cel crushing, in the range of 20 - 40 mass %, the quick extrusion rate of an EVA addition became possible especially good compared with other range, and it resulted in it being excellent in productivity. Moreover, it also turns out that warm air cooling is needed according to the rise of the extrusion rate of a honeycomb Plastic solid from Table 2.
[0041]
[Effect of the Invention] It can mass-produce efficiently, without according to this invention, producing a crack for the honeycomb Plastic solid which has a thin septum of 25-100 micrometers, or making the mouthpiece for extrusion molding transform. Moreover, according to this invention, improvement in the firmness of a honeycomb Plastic solid and gestalt stability can be aimed at by specifying the mixing ratio of the wax which is a shaping binder, and thermoplastics.

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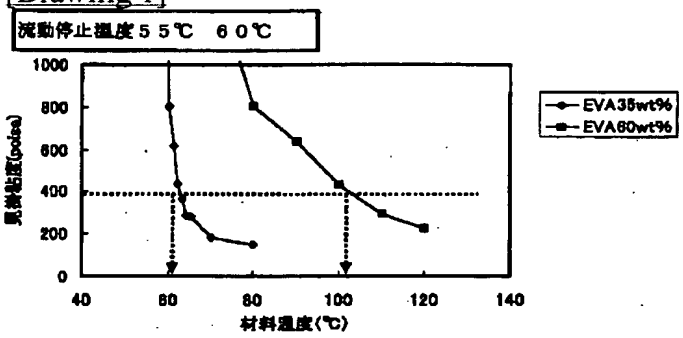
DRAWINGS

[Drawing 1]



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